Chemically synthesis of Metal Sulphide based Electrodes for supercapacitor

Synopsis in Candidature for the Degree of

Doctor of Philosophy in Physics

Submitted by

Mr. Bharat Venkatrao Bhagnure

Under the Guidance of

Dr. Shyam K. Gore

Dnynopasak College Jintur

Submitted to

स्वामी रामानंद तीर्थ मराठवाडा विद्यापीठ, नांदेड.

Swami Ramanand Teerth Marathwada University, Nanded

2020-2021

1. Introduction

Energy is one of the most vital issues to address the deterioration of nature and depletion of fossil fuels. The need for effective and efficient energy conversion/storage devices has motivated scientists to design competent clean energy storage devices that will be beneficial for society. The global energy demand has been swelling rapidly and it is estimated that within the next 15 years the energy demand will be double. Energy and the environment are among the most important concerns of the current age. However, until now most of the total energy comes from fossil fuels that are unsustainable as there are finite reserves. Therefore, energy conversion from renewable sources has been considered as an encouraging solution to significantly reduce the dependency on fossil fuels. Electrochemical supercapacitors (ESs) are one of these energy storage devices having a high power density of (>10 kW kg^{-1}), fast charging, and stable cycle life and hence are considered as potential candidates for next-generation flexible storage devices [1-7]. ESs are mainly classified into electric double-layer capacitors that are based on non-faradic processes involving adsorption/desorption of ions/molecules/species, breaking/creation of chemical bonds, phase transitions, and pseudocapacitors that are based on faradic processes. ESs are also categorized into two types, symmetric (SC) and asymmetric (ASC) in accordance with the arrangement of electrodes. The SC supercapacitors have both anodes and cathodes identical to each other, whereas the ASC supercapacitors are made of unlike electrodes, irrespective of the charge storage mechanism (faradaic or non-faradaic). The ASC supercapacitor has emerged as the most desirable energy storage device with a wider potential range. The ESs are characterized by their energy density values which are based on the total specific capacitance (C) and total cell voltage (V) of the device and are obtained by equation $E = 1/2\ CV^2$ [3-5]. ESs are based on the principle of simple charge separation at the interface between the electrode and an electrolyte, which helps to accumulate and deliver energy at relatively higher rates.

Metal oxides (MOs)/hydroxides, metal sulfides (MSs), MXenes, transition metal chalcogenides, conducting polymers, and different carbon-based materials such as activated carbon, carbon aerogel, graphene, and carbon nanotubes with high surface area, high specific capacitance, and good conductivity are developed [4-7]. Recently, MSs have gained major attention as electrode materials owing to their unique electrochemical properties, low cost, high abundant production, and high theoretical capacities, making them potential substitutes for noble metals in a range of fields with high effectiveness.

2. Literature Review

Until now, a variety of materials, such as conducting polymers, carbon-based materials, and transition metal oxides/hydroxides have been studied intensively as efficient electrode materials for ESs and quantum-dot sensitized solar cells (QDSSCs). Transition metal oxides, including MnO_2 and RuO_2, are the most promising electrode materials for ESs owing to their remarkably high specific capacitance (theoretical value of ~1370 F g^{-1} for MnO_2 and 1500-2200 F g^{-1} for RuO_2), reversible charge-discharge features, wide potential window, and good electrical conductivity of ~105 S cm^{-1} for RuO_2 [8-10]. On the other hand, the poor electronic conductivity (10−5–10−6 S cm−1) and low rate performance of MnO_2, and the high processing and material costs of RuO2 electrode materials seriously restrict their practical applications [11]. The major disadvantages such as the low electrical conductivity of transition metal oxides, which increases the overall resistance of the device, the poor cycling stability of conducting polymers, low specific capacitance of carbon-based materials, the difficult synthesis of transition metal nitrides due to the formation of NRN bonds, and the instability in air and humid atmosphere [12-13]. Nevertheless, it is essential to synthesize other efficient electrode materials with desirable electrochemical properties, such as good electrochemical stability, porous structure, and high electrical conductivity to further enhance the performance of ESs.

In recent years, transition metal sulfides (TMS) have attracted increasing attention as electrode materials owing to their unique electrochemical properties, low cost, abundance, stress-free production, and high theoretical capacities, making them potential substitutes for noble metals in a range of fields with high effectiveness [14-15]. The structure, profile, and particle size of the TMS have an important effect on the electrocatalytic applications and catalytic performance of metals. TMS electrode materials exhibit higher conductivity than that of TMO because of their narrow bandgap and the faradic reaction being involved in the charge–discharge process [16]. In particular, the electrochemical activity of TMS (transition metal sulphide) is higher than that of TMO (transition metal oxide) due to the substitution of oxygen with sulfur atoms, which possess higher ionic conductivity [17]. In addition, TMS has greater ionic diffusivity due to their higher anionic polarizability, which arises from the larger size of S^{2-} ions. Among the TMS investigated, cobalt sulfide (CoS), copper sulfide (CuS), iron sulfide (FeS), and nickel sulfide (NiS) are important multifunctional semiconductors with potential applications in solar energy devices, lithium-ion batteries, and gas sensors because of their high activity [18].

To the best of our knowledge, there have been very few studies on the application of these MS in ESs. Therefore, we will have synthesized MS electrodes using one of the appropriate chemical methods for ESs device fabrication.

3. Objective

The main objective of this synopsis to develop and synthesis metal sulphide those have different phases and supercapacitor application to enhance the performance. Materials includes metal sulphide.

- Synthesis of metal sulphides electrodes nanostructure using various chemical synthesis methods.
- Structural and morphological properties of the prepared nanostructured electrodes will be studied using various characterization techniques such as X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), high resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, etc.
- Electrochemical performance will be studied in various electrolyte solutions.
- Rate capability and capacitance retention will be studied.
- Symmetric/asymmetric device will be fabricated.

4. Methodology

There are several methods in the literature for the synthesis of metal sulphide such as CBD, SILAR, hydrothermal method, which is reliable and easy to synthesis of metal sulphide. Among these method one of the synthesis methods will be used to synthesized metal sulphide.

4.1 CBD (Chemical bath deposition)

Chemical bath deposition (CBD) is widely used for the deposition of various metal chalcogenide thin films. It produces good deposits on suitable substrates by the controlled precipitation of the compounds from the solution. It does not require high voltage equipment, works at room temperature, and hence it is inexpensive. The only requirement for this deposition route is an aqueous solution consisting of a few common chemicals and a substrate for the film to be deposited. By optimizing CBD preparative parameters, such as deposition temperature, time,

pH, complexing agent etc. transition metal sulphide films were prepared. The metal sulphide films were deposited from the solution containing precursor by using different complexing.

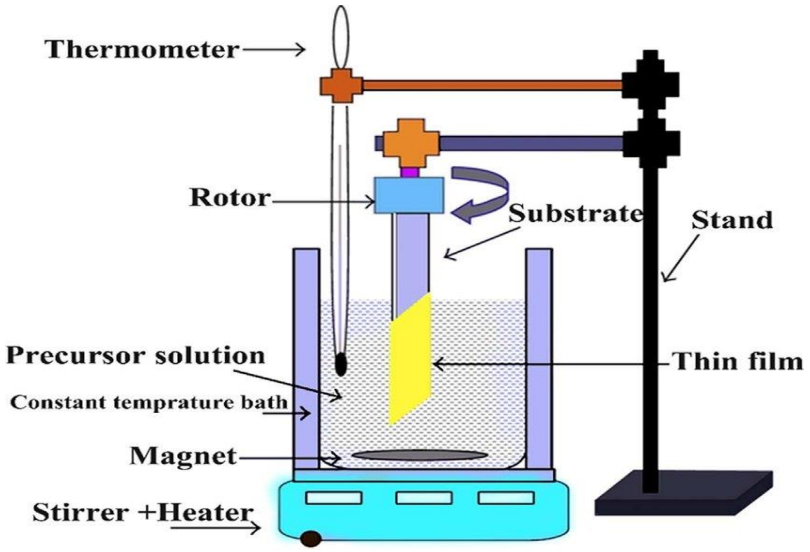

Fig.1. Instrumental details of CBD

4.2 SILAR (successive ionic layer adsorption and reaction)

Successive ionic layer adsorption and reaction (SILAR) method is relatively simple and offers wide range of advantages over other expensive methods of thin film deposition.

1. It is a process in which the deposition rate and thickness of the film can be easily controlled over a wide range by changing the deposition cycles.
2. Relatively uniform films can be obtained on substrates of any shape, there is no restriction on substrate material, dimensions or its surface profile.
3. Unlike vacuum based deposition method, SILAR method does not require any expensive and sophisticated instruments and also vacuum at any stage which is a great advantage in the context of an industrial application.
4. The SILAR method usually require low operating temperature.

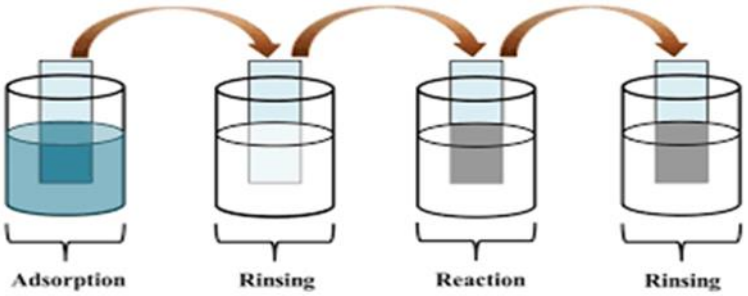

Fig.2. Schematic representation of SILAR method

4.3 Hydrothermal

Many types of nanomaterial have been successfully synthesized by using hydrothermal method. Nanomaterial with high vapor pressures can be produced by the hydrothermal method with minimum loss of materials. The compositions of nanomaterial to be synthesized can be well controlled in hydrothermal synthesis through liquid phase or multiphase chemical reactions.

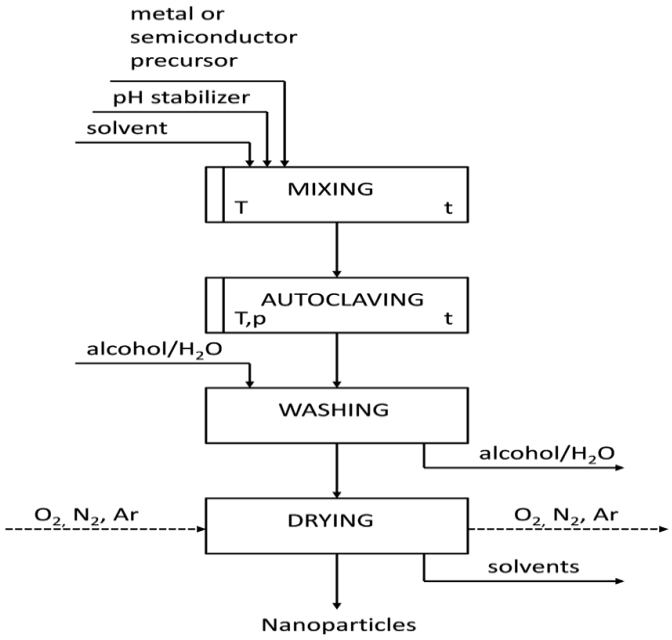

Fig.3. Block diagram of hydrothermal.

4.4. Materials characterizations

A concise account of the instruments and techniques used for acknowledgement of structural, morphological, electrochemical properties, are discussed in this section.

4.4.1 Structural studies

X-ray diffraction (XRD) technique is a one of the influential, renowned and most appropriate techniques for structural revelation of materials prepared in the form of films or powders.

4.4.2 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique used to observe vibration, rotational, and other low-frequency modes in a system.

4.4.3 Fourier Transform Infrared Spectroscopy

FT-IR spectroscopy is a tool for investigation of the various chemical groups present in the sample material.

4.4.4 Morphological studies

Field Emission Scanning Electron Microscopy is a tool for investigation of the surface morphology and posture of the sample material.

4.4.5 High Resolution Transmission Electron Microscopy (HR-TEM)

HR-TEM is one of most powerful techniques used in the characterization of Nanocomposites. It has capacity to inspect the constitutional characteristics of Nanocomposites such as grain shape and size, crystallinity and chemical variations at a nanometer scale resolution.

4.4.6 Electrochemical analysis

The cyclic voltammetry (CV), Galvanostatic charge-discharge (GCD), stability, rate capability, and impedance spectroscopy will be measured using electrochemical work station.

4.5. Work plan

The proposed work will be carried out in following phases:

Phase – I (First Year)

- In the first year, literature survey will be carried out. The various metal sulphides will be prepared using suitable synthesis method.

Phase – II (Second Year)

- The electrochemical performance of the prepared metal sulphides will be measured and studied in different electrolyte such as KOH, H_2SO_4, NaOH, KCL, etc.

Phase – III (Third Year)

- To the study the industrial potential of the prepared metal sulphides, the symmetric /asymmetric device will be fabricated.
- The work will be communicated time to time with the high impact journals.

5. Reference

1. C. Brown, S. Chandrasekaran, S. Chen, L. Deng, Z. Lin, F. Peng, L. Yao, Y. Zhang, Chem. Soc. Rev 48 (2019) 4178-4280.
2. X. Rui, H. Tan, Q. Yan, Nanoscale, 48 (2014) 9889-9924.
3. R. Attias, D. Aurbach, A. Borenstein, T. Brousse, O. Hanna, S. Luski, J Mater A, 118 (2017) 12653-12672.
4. B. Dunn, F. M. El-Kady, R. B. Kaner, Y. Shao, J. Sun, H. Wang, Q. Zhang, M. Zhu, Chem A, 118 (2018) 9233-9280.
5. Y. Gogotsi, R. Penner, ACS Nano, 12 (2018) 2081-2083.

6. N. Choudhary, C. Li, J. Moore, N. Nagaiah, J. Thomas, L. Zhai, Adv. Mater. 29 (2017) 1605336.
7. Y. Song, Y. Wang, Y. Xia, Chem. Soc. Rev. 45 (2016) 5925−5950.
8. Z. J. Han, S. Pineda, A. T. Murdock, D. H. Seo, K. Ostrikov and A. Bendavid, J. Mater. Chem. A, 2017, 5, 17293
9. A. V. Radhamani, K. M. Shareef and M. S. R. Rao, ACS Appl. Mater. Interfaces, 2016, 8, 30531.
10. H. Xia, D. Zhu, Z. Luo, Y. Yu, X. Shi, G. Yuan and J. Xie, Sci. Rep., 2013, 3(2978), 1.
11. K. D. Ikkurthi, S. S. Rao, M. Jagadeesh, A. E. Reddy, T. Anitha, H. J. Kim, New J. Chem., 42 (2018) 19183.
12. W. Li, S. Wang, L. Xin, M. Wu and X. Lou, J. Mater. Chem. A, 2016, 4, 7700.
13. T. Lv, Y. Yao, N. Li and T. Chen, Angew. Chem., Int. Ed., 2016, 55, 9191.
14. Z. Li, J. Han, L. Fan and R. Guo, CrystEngComm, 2015, 17, 1952.
15. N. Li, T. Lv, Y. Yao, H. Li, K. Liu and T. Chen, J. Mater. Chem. A, 2017, 5, 3267.
16. S. Sahoo, R. Mondal, D. J. Late and C. S. Rout, Microporous Mesoporous Mater., 2017, 244, 101.
17. T. Zhu, Z. Wang, S. Ding, J. S. Chen and X. W. Lou, RSC Adv., 2011, 1, 397.
18. X. Yang, L. Zhao and J. Lian, J. Power Sources, 2017, 343, 373

Signature
Research Student

Signature
Research Supervisor/Guide/Co-guide